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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Polyaddition Products Containing Hydroxyl and Uretdione Groups, Process for Their Preparation, Their Use for the Production of Highly Reactive Polyurethane Powder Coatings Which are Free

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Industrie Canada Industry Canada

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Abstract:

Polyaddition products containing hydroxyl and uretdione groups, a process for their preparation, their use for the production of highly reactive polyurethane (PUR)
5 powder coatings which are free from elimination products and which crosslink to give light-stable and weather-stable coating films of high gloss, and the powder coatings produced accordingly.

Polyaddition products containing hydroxyl and uretdione groups, process for their preparation, their use for the production of highly reactive polyurethane powder coatings which are free from elimination products, and the
5 polyurethane powder coatings produced accordingly

Polyaddition products containing hydroxyl and uretdione groups, a process for their preparation, their use for the production of highly reactive polyurethane (PUR) powder coatings which are free from elimination products
10 and which crosslink to give light-stable and weather-stable coating films of high gloss, and the powder coatings produced accordingly.

DE-C 30 30 572 presents a process for the preparation of polyaddition products which contain uretdione groups, and
15 the products prepared accordingly. These are reaction products of the isocyanurate-free uretdione (UD) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (also called isophorone diisocyanate or IPDI for short) - which can be prepared according to DE-C 30 30 513 or
20 DE-C 37 39 549 - with diols and, if desired, monoalcohols or monoamines. The reaction can be carried out in bulk or else in the presence of appropriate solvents. So far, in practice, this class of crosslinking agent has been produced in economically significant, saleable quantities
25 only in a suitable solvent under mild conditions, at about 60°C, so as to avoid heat-induced ring opening during the synthesis. Preparation in bulk has not previously gone beyond the laboratory scale, since a high level of viscosity develops during the reaction as a
30 function of the molecular mass of the crosslinking agent; increasing the temperature as a means of controlling viscosity is, as indicated in DE-C 30 30 572, a limited measure.

This limit is also evident from the examples of
35 DE-C 30 30 572: it is situated at a molecular weight of

not more than 3 000 or at a uretdione/diol molar ratio of 5:4 for a uretdione grade having a free NCO content of 17 and a total NCO content of 37.8% by weight. If the free NCO content of the isophorone diisocyanate uretdione increases for a constant total NCO content, i.e. there is a simultaneous decrease in the degree of oligomerization and thus also in the molecular mass of the uretdione employed, then there is a corresponding decrease in the molecular mass of the uretdione group-containing polyaddition products. For the reasons given above, there seems little point in the preparation of uretdione group-containing polyaddition products of high molecular mass in the context of their application as crosslinking agents for the production of PUR powder coatings. This is also reflected in DE-C 30 30 539 and DE-C 30 30 588.

In DE-C 30 30 539 the molecular weights claimed are between 550 and 4 300, preferably between 1 500 and 2 000, and the uretdione/diol molar ratios are between 2 : 1 and 6: 5, preferably between 3 : 2 and 5 : 4.

In DE-C 30 30 588 the claimed molecular weights are very similar, namely from 500 to 4 000, preferably between 1 450 and 2 800 at a uretdione/diol molar ratio comparable with that of DE-C 30 30 539.

Decisive disadvantages of the PUR powder coatings in accordance with the teaching of DE-C 30 30 539 and DE-C 30 30 588, which are free from elimination products, were the limited possibilities for combination with polymers containing hydroxyl groups. Firstly - DE-C 30 30 539 - high functionalities of from ≥ 3.4 to ≤ 7 , preferably from 3.7 to 4.5, were necessary. In order to achieve the high crosslinking density for high-quality PUR powder coatings, it was necessary to compensate for the chain-terminating components of the crosslinking agent. Secondly - DE-C 30 30 588 - it was necessary to take account of the free NCO content of the crosslinking agents in so far as the functionality of the hydroxyl

group-containing polymers is to be adapted to the free NCO content in order to avoid gelling during extrusion, and therefore to suppress losses in the quality of the coatings. It was necessary to limit the OH functionality to from ≥ 2.2 to ≤ 3.5 , preferably from 2.5 to 3.4. Complex investigation was and still is necessary in order to tailor the resin and curing agent to one another.

In DE-C 30 30 572, polyaddition products which contain uretdione groups and terminal OH groups are described in one example and are claimed. The scope corresponds to the polyaddition product specified above. However, the OH-terminal polyaddition products have so far acquired no importance in the PUR powder coating sector, since there was no economic value in comparison with the other crosslinking agents; see Example 5 of DE-C 30 30 572 in comparison with the remaining examples. The numbers speak for themselves. These and chemical reasons, namely the uncontrolled polyaddition of the free OH groups with NCO groups, which are additionally produced by uretdione cleavage during the synthesis, were good arguments to attach no importance to this kind of crosslinking agent.

The object of the present invention was therefore to discover polyaddition products which contain hydroxyl and uretdione groups, in order to use these crosslinking agents for the production of PUR powder coatings which are free from elimination products, and the invention also relates to the PUR powder coatings produced accordingly, which no longer have the abovementioned disadvantages of the prior art.

- Surprisingly, polyaddition products containing hydroxyl and uretdione groups and having high molecular masses have now been found which are obtainable by reacting
- I. from 40 to 85% by weight of the uretdione of isophorone diisocyanate and
 - II. from 60 to 15% by weight of diols and/or chain extenders,

the polyaddition products carrying terminal hydroxyl groups, having a functionality of 2 and molecular masses of between 4 500 and 10 000, preferably between 5 500 and 7 000, and reaction being possible either in solvent or, in particular, without solvent.

It was surprising, furthermore, that these polyaddition products having a molecular mass $> 4\,500$ can be formulated, in combination with hydroxyl group-containing polymers, to give PUR powder coatings which, as a particularly surprising feature, possess heightened reactivity and lead to a gloss which is outstanding for PUR powder coatings.

The present invention accordingly relates to polyaddition products which contain hydroxyl and uretdione groups and are produced from the uretdione of isophorone diisocyanate and diols and/or chain extenders, according to Claim 1.

The invention also relates to the use of the polyaddition products in transparent or pigmented PUR powder coatings of high reactivity and excellent gloss which are free from elimination products and which are produced from the bifunctional polyaddition products, free of blocking agents and containing hydroxyl and uretdione groups, and from hydroxyl group-containing polymers and the additives customary in PUR chemistry.

The isocyanurate-free uretdione of isophorone diisocyanate is highly viscous at room temperature with a viscosity of greater than 10^6 mPa·s; at 60°C the viscosity is $13 \cdot 10^3$ mPa·s and at 80°C it is $1.4 \cdot 10^3$ mPa·s. The free NCO content is between 16.8 and 18.5% by weight, denoting that more or less high proportions of polyuretdione of IPDI must be present in the reaction product. The monomer content is $\approx 1\%$. The total NCO content of the reaction product after heating at $180 - 200^\circ\text{C}$ is 37.5 - 37.8% by weight.

- Diols which are suitable for the preparation of the polyaddition products according to the invention, these products containing hydroxyl and uretdione groups, are all those customarily employed in PUR chemistry; however, particular preference is given in this case to ethylene glycol (E), butane-1,4-diol (B), pentane-1,5-diol (P), hexane-1,6-diol (HD), 3-methylpentane-1,5-diol (Pm), 2,2,4(2,4,4)-trimethylhexanediol (TMH-d) and neopentylglycol hydroxypivalate (Eg).
- 10 The polyaddition products of the invention advantageously contain chain extenders in the form of linear polyesters which contain hydroxyl groups and have a molecular mass between 250 and 2 000, preferably from 300 to 1 500. They are prepared by, for example, combination of diols and dicarboxylic acids.

To prepare the chain extenders - linear polyesters containing hydroxyl groups - it is preferred to employ not only the abovementioned diols but also 2-methylpropanediol, 2,2-dimethylpropanediol (NPG), diethylene glycol, dodecane-1,12-diol (C₁₂) and trans- and cis-cyclohexanedimethanol (CHDM).

The preferred dicarboxylic acids include aliphatic and optionally alkyl-branched acids such as succinic, adipic (As), suberic, azelaic and sebacic (Sb) acid, and 2,2,4(2,4,4)-trimethyladipic acid; also included are lactones and hydroxycarboxylic acids, such as ε-caprolactone and hydroxycaproic acid.

The diol/chain extender mixtures of the invention are employed in a ratio of from 5 : 95 to 90 : 10. The products of the invention can be prepared either in solvent or in bulk, i.e. without solvent.

The polyaddition products according to the invention can be obtained, inter alia, by the process described below.

The reaction in solvent is in general carried out at temperatures of from 50 to 100°C, preferably between 60 and 90°C. The OH component, diols and/or chain extenders, is taken as initial charge and the uretdione is added as rapidly as possible without the reaction temperature exceeding the limit specified above. The reaction is complete after from 30 to 150 minutes. Subsequently the solvent is removed. Apparatus suitable for this purpose includes evaporation screws, filmtruders or, alternatively, spray-dryers.

Suitable solvents are benzene, toluene or other aromatic or aliphatic hydrocarbons, acetates such as ethyl or butyl acetate, ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone, or chlorinated aromatic and aliphatic hydrocarbons, as well as any desired mixtures of these or other inert solvents.

Furthermore, the invention relates to the solvent-free and continuous preparation of the process products by means of intensive kneading in a single- or multi-screw extruder, in particular in a twin-screw extruder. The solvent-free synthesis requires temperatures of significantly > 120°C to 190°C. It came as a surprise that temperatures this high could be used for the uretdione syntheses. These temperatures are well within the range in which uretdiones unblock, meaning that high contents of free isocyanate can occur and thus that uncontrolled reaction processes were to be expected. This fact was significant for the synthesis of uretdione polyaddition products containing hydroxyl groups, and it was all the more surprising that this synthesis should be carried out. Factors which proved advantageous in this synthesis were the short reaction times of < 5 minutes, preferably < 3 minutes, especially < 2 minutes. A further principle is that the short exposure to heat is sufficient to give a homogenous mixture of the reactants and to cause them to react completely or very substantially. Subsequently, controlled cooling is carried out in

accordance with the development of equilibrium, and, if necessary, the reaction is taken to completion.

The reaction products are supplied to the kneading apparatus in separate product streams; it is possible to
5 preheat the starting components at up to 100°C, preferably up to 80°C. If there are more than two product streams, then these can also be metered in batches. Diol and/or chain extender and/or catalysts and/or other conventional coatings additives, such as levelling agents
10 and/or stabilizers, can be combined into one product stream; the same applies to those which are inert towards isocyanate groups: catalysts and, correspondingly, the abovementioned coatings additives.

Similarly, the sequence of the product streams can be
15 varied, and the point of entry for the product streams may be different.

Known processes and technologies are used for the secondary reaction, cooling, comminution and bag-filling.

In order to accelerate the reaction of polyaddition, it
20 is also possible to use the catalysts which are customary in PUR chemistry. They are employed in a concentration of from 0.01 to 1% by weight, preferably from 0.03 to 0.5% by weight, based on the reaction components employed. Catalysts which have proven particularly suitable so far
25 are tin(II) and tin(IV) compounds. Particular mention is made here of dibutyltin dilaurate (DBTL). However, other catalysts would not be regarded as unsuitable per se.

The present invention relates, furthermore, to the use of the polyuretdione addition products according to the
30 invention, containing hydroxyl and uretdione groups, in PUR powder coatings, which are surprisingly distinguished by heightened reactivity. Entirely surprisingly, therefore, the curing conditions can be reduced distinctly in comparison with those known hitherto, which is signifi-

cant both on economic and on ecological grounds.

The present invention further relates to polyurethane powder coatings which are free from elimination products and which comprise the polyaddition products according to
5 the invention in combination with hydroxyl group-containing polymers. Suitable co-reactants for PUR powder coatings are compounds which contain those functional groups which react with isocyanate groups during the curing process as a function of temperature and time, for
10 example hydroxyl, carboxyl, mercapto, amino, urethane and (thio)urea groups. Polymers which can be employed are addition polymers and condensation polymers.

Preferred components are primarily polyethers, polythioethers, polyacetals, polyesteramides, epoxy resins
15 containing hydroxyl groups in the molecule, amino resins and their modification products with polyfunctional alcohols, and also polyazomethines, polyurethanes, polysulphonamides, melamine derivatives, cellulose esters and ethers partially hydrolysed homo- and copolymers of
20 vinyl esters, but especially polyesters and acrylate resins.

Carboxylic acids which are preferred for the preparation of polyesters may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic in nature and may if desired be
25 substituted by halogen atoms and/or unsaturated. Examples are succinic, adipic (As), suberic, azelaic, sebacic, phthalic, terephthalic (Ts), isophthalic (Is), trimellitic, pyromellitic, tetrahydrophthalic, hexahydrophthalic, hexahydroterephthalic, di- and tetrachloro-
30 phthalic, endomethylenetetrahydrophthalic, glutaric, maleic and fumaric acid and - where accessible - their anhydrides, dimethyl terephthalate (DMT), bisglycol terephthalate, and also cyclic monocarboxylic acids such as benzoic acid, p-tert.-butylbenzoic acid or hexahydro-
35 benzoic acid.

Examples of suitable polyhydric alcohols are ethylene glycol, 1,2-propylene glycol and 1,3-propylene glycol, 1,4-butylene glycol and 2,3-butylene glycol, di- β -hydroxyethylbutanediol, hexane-1,6-diol, octane-1,8-diol, 5 neopentylglycol, cyclohexanediol, 1,4-bis(hydroxymethyl)-cyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, 2,2-bis[4-(β -hydroxyethoxy)phenyl]propane, 2-methylpropane-1,3-diol, 3-methylpentane-1,5-diol, 2,2,4(2,4,4)-trimethylhexane-1,6-diol, glycerol, trimethylolpropane, 10 trimethylolethane, hexane-1,2,6-triol, butane-1,2,4-triol, tris(β -hydroxyethyl) isocyanurate, pentaerythritol, mannitol and sorbitol, and also diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, polypropylene glycols, polybutylene glycols, 15 xylylene glycol and neopentylglycol hydroxypivalate.

Mono- and polyesters can also be employed as lactones, for example ϵ -caprolactone, or hydroxycarboxylic acids, for example hydroxypivalic acid, ω -hydroxydecanoic acid, ω -hydroxycaproic acid and thioglycolic acid. Also 20 suitable are polyesters of the abovementioned polycarboxylic acids or their derivatives with polyphenols, such as hydroquinone, bisphenol A, 4,4'-dihydroxybiphenyl or bis(4-hydroxyphenyl) sulphone; polyesters of carbonic acid obtainable from hydroquinone, diphenylolpropane, p-xylylene glycol, ethylene glycol, butanediol or hexane- 25 1,6-diol and other polyols by conventional condensation reactions, for example with phosgene or diethyl or diphenyl carbonate, or from cyclic carbonates such as glycol carbonate or vinylidene carbonate, by polymeriza- 30 tion in a known manner; polyesters of silicic acid, polyesters of phosphoric acid, for example from methane-, ethane-, β -chloroethane-, benzene- or styrenephosphoric acid or the corresponding phosphoryl chlorides or phosphoric esters and polyalcohols or polyphenols of the 35 type mentioned above; polyesters of boric acid; polysiloxanes, for example the products which are obtainable by a hydrolysis of dialkyldichlorosilanes with water followed by treatment with polyalcohols and the products

obtainable by addition reaction of polysiloxane dihydrides with olefins such as allyl alcohol or acrylic acid.

5 Other examples of preferred polyesters are the reaction products of polycarboxylic acids with glycidyl compounds, as described, for example, in DE-C 24 10 513.

10 The hydroxyl group-containing polyesters which are employed with particular preference have an OH functionality of > 2 , an OH number of from 20 to 200 mg of KOH/g, preferably from 30 to 150 mg of KOH/g, a viscosity of $< 60\,000$ mPa·s, preferably $< 40\,000$ mPa·s at 140°C and a melting point of $> 70^{\circ}\text{C}$ to $\leq 120^{\circ}\text{C}$, preferably from 75°C to 100°C .

15 Examples of glycidyl compounds which can be used are esters of 2,3-epoxy-1-propanol with monobasic acids having from 4 to 18 carbon atoms, such as glycidyl palmitate, glycidyl laurate and glycidyl stearate, alkylene oxides having from 4 to 18 carbon atoms, such as butylene oxide, and glycidyl ethers such as octyl glycidyl ether.

The dicarboxylic acids which can be used in this process are all those polycarboxylic acids listed below under 2; it is also possible to employ monocarboxylic acids, which are listed under 3 by way of example.

25 Other preferred components are monomeric esters, for example bis(hydroxy(alcohol))esters of dicarboxylic acids, esters of monocarboxylic acids with polyols having a functionality of more than two, and oligo esters which can be prepared by condensation reactions from the raw materials which are customary in paint chemistry.

30 Examples of materials regarded as customary are:

1. alcohols having 2 to 24, preferably 2 to 10, carbon atoms and 2 to 6 OH groups which are attached to

- 5 nonaromatic carbon atoms, for example ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, butanediols, neopentylglycol, hexanediols, hexanetriols, perhydrobisphenol, dimethylolcyclohexane, glycerol, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol and mannitol;
- 10 2. di- and polycarboxylic acids having 4 to 36 carbon atoms and 2 to 4 carboxyl groups, and esterifiable derivatives thereof, such as anhydrides and esters, for example phthalic acid (anhydride), isophthalic acid, terephthalic acid, alkyltetrahydrophthalic acids, endomethylenetetrahydrophthalic anhydride, adipic acid, succinic acid, maleic acid, fumaric acid, dimeric fatty acids, trimellitic acid, pyromellitic acid and azelaic acid;
- 15 3. monocarboxylic acids having 6 to 24 carbon atoms, for example caprylic acid, 2-ethylhexanoic acid, benzoic acid, p-tert.-butylbenzoic acid, hexahydrobenzoic acid, mixtures of monocarboxylic acids from natural oils and fats, such as coconut fatty acid, soya-oil fatty acid, castor oil fatty acid, hydrogenated and isomerized fatty acids, such as "Konjuvandol" fatty acid and mixtures thereof; it is also possible to employ the fatty acids as glycerides and to react them by transesterification and/or dehydration;
- 20 4. monohydric alcohols having 1 to 18 carbon atoms, for example methanol, ethanol, isopropanol, cyclohexanol, benzyl alcohol, isodecanol, nonanol, octanol and oleyl alcohol.
- 30

The polyesters can be obtained in a manner known per se by condensation in an inert gas atmosphere at temperatures from 100 to 260°C, preferably from 130 to 220°C, in the melt or in an azeotropic procedure, as described in,

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for example, Methoden der Organischen Chemie [Methods in Organic Chemistry] (Houben-Weyl), volume 14/2, 1 - 5, 21 - 23, 40 - 44, Georg Thieme Verlag, Stuttgart, 1963 or in C.R. Martens, Alkyd Resins, 51 - 59, Reinhold Plastics
5 Appl. Series, Reinhold Publishing Comp., New York, 1961.

Preferred acrylate resins for possible use as OH components are homo- or copolymers, examples of monomers which can be selected as starting products being the following: esters of acrylic acid and methacrylic acid
10 with dihydric, saturated, aliphatic alcohols having 2 to 4 carbon atoms, for example 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 4-hydroxybutyl acrylate and the corresponding methacrylates; alkyl acrylates and methacrylates having 1 to 18 carbon atoms in the alcohol
15 components, for example methyl acrylates, ethyl acrylates, propyl acrylate, isopropyl acrylate, n-butyl acrylate, tert.-butyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate and the corresponding methacrylates; cyclohexyl acrylate and methacrylate; acrylonitrile and
20 methacrylonitrile, acrylamide and methacrylamide; and N-methoxymethyl(meth)acrylamide.

Particularly preferred acrylate resins are copolymers of

- a. from 0 to 50% by weight of esters of acrylic or methacrylic acid with dihydric or polyhydric
25 alcohols, such as 1,4-butanediol monoacrylate, hydroxypropyl (meth)acrylate; and also vinyl glycol, vinylthioethanol, allyl alcohol and 1,4-butanediol monovinyl ether;
- b. from 5 to 95% by weight of esters of acrylic acid or
30 methacrylic acid with monohydric alcohols containing from 1 to 12 carbon atoms, for example methyl methacrylate, ethyl acrylate, n-butyl acrylate or 2-ethylhexyl acrylate;
- c. from 0 to 50% by weight of aromatic vinyl compounds,

such as styrene, methylstyrene or vinyltoluene;

- d. from 0 to 20% by weight of other monomers having functional groups, for example acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, maleic anhydride, maleic acid monoesters, acrylamide, methacrylamide, acrylonitrile or N-methylol(meth)acrylamide and glycidyl (meth)acrylate, the proportion of group a. and/or b. being at least 5% by weight.
- 10 The acrylate resins can be prepared by the conventional methods, i.e. by a solution, suspension, emulsion or precipitation polymerization, but preferably by bulk polymerization which, in turn, can be initiated by UV light.
- 15 Further polymerization initiations which are used are the conventional peroxides or azo compounds, for example dibenzoyl peroxide, tert.-butyl perbenzoate or azobisisobutyronitrile. The molecular weight can be regulated using, for example, sulphur compounds such as tert.-
- 20 dodecanethiol.
- Preferred polyethers can be prepared, for example, by the polyaddition of epoxides, such as ethylene oxide, propylene oxide, butylene oxide, trimethylene oxide, 3,3-bis(chloromethyl)oxacyclobutane, tetrahydrofuran, styrene oxide, the bis(2,3-epoxypropyl) ether of diphenylolpropane or epichlorohydrin with itself, for example in the presence of BF_3 , or by the addition of these epoxides, if desired as a mixture or in succession, with starting components containing reactive hydrogen
- 25 atoms, such as alcohols or amines, for example water, ethylene glycol, 1,3-propylene glycol or 1,2-propylene glycol, pentamethylene glycol, hexanediol, decamethylene glycol, trimethylol propane, 4,4'-dihydroxydiphenylpropane, aniline, ammonia, ethanolamine, ethylenediamine,
- 30 di(β -hydroxypropyl)methylamine, di(β -hydroxyethyl)ani-

line, hydrazine, and also hydroxyalkylated phenols, for example di(β -hydroxyethoxy)resorcinol.

It is also possible to employ polyureas and/or polyurethanes containing hydroxyl groups.

- 5 As polymers containing hydroxyl groups it is also possible, of course, to employ mixtures of two or more substances.

10 The ratio in which the hydroxyl group-containing polymers and the polyaddition products containing hydroxyl and uretdione groups (crosslinking agents) are mixed is generally selected such that 0.5 - 1.2, preferably 0.8 - 1.1, especially preferably 1.0 NCO group is present per OH group.

15 For the production of PUR powder coatings, the isocyanate component is mixed and homogenized in the melt with the appropriate hydroxyl group-containing polymer and, if desired, catalysts, pigments and conventional auxiliaries, such as fillers and levelling agents, for example silicone oil, and acrylate resins. This can be
20 carried out in suitable apparatus, for example heatable kneading apparatus, but preferably by extrusion, in which context upper temperature limits of from 130 to 140°C should not be exceeded. After the extruded composition has been cooled to room temperature and comminuted
25 appropriately, it is ground to give the ready-to-spray powder. The application of the ready-to-spray powder to suitable substrates can be carried out by the known processes, for example by electrostatic powder spraying, fluidized-bed sintering, or electrostatic fluidized-bed
30 sintering. After the application of the powder, the coated workpieces are heated for curing purposes for from 60 to 4 minutes at a temperature of from 150 to 220°C, preferably for from 30 to 6 minutes at from 160 to 200°C.

The subject-matter of the invention is illustrated in

more detail below using examples.

A Preparation of the polyaddition products according to the invention, containing hydroxyl and uretdione groups

5 A 1 Polyol chain extenders

General preparation procedure

10 The starting components - see Table 1 - are placed in a reactor and heated to $\approx 140^{\circ}\text{C}$ using an oil bath. After the substances have very largely melted, 0.1% by weight of di n-butyltin oxide is added as catalyst. Elimination of water begins at 150 to 160°C . Over the course of 2 to 3 hours the temperature is raised to 180°C to 190 $^{\circ}\text{C}$ and the esterification is brought to an end
15 over a further 8 to 10 hours. Throughout the reaction period the bottom product is stirred and a gentle stream of nitrogen is passed through the reaction mixture. The acid number of the polyesters was in each case < 2 mg of KOH/g.

Table 1: Polyol chain extenders

Example A 1	Starting components in mole				Characteristics	
	As	Sb	NPG	P	HD	OH number mg KOH/g
1	1		2			335 \pm 15 \approx 1 500
2	1.25		2.25			290 \pm 10 \approx 1 950
3	1			2		335 \pm 15 \approx 1 270
4		1	2			289 \pm 10 \approx 1 150
5	4		3		2	106 \pm 7 \approx 3 500
6	Polycaprolactones from Interlox-Capa 200					216 Melting range 18 - 23 °C
7	Polycaprolactones from Interlox-Capa 210					112 Melting range 30 - 40 °C

A 2 Polyaddition products containing hydroxyl and uretdione groups

General preparation procedures

A 2.1 from solvent

5 The polyol component - see Table 2 - and the
catalyst (0.03 - 0.5% by weight of DBTL), in
solution in a solvent, are placed in the reactor.
With vigorous stirring and under an inert gas
10 atmosphere, the calculated quantity of IPDI
uretdione, in solution in the solvent, is added
at a rate such that the reaction temperature does
not exceed 100°C. The reaction is monitored by
means of titrimetric determination of NCO and is
15 complete after 1 to 3 hours. The solvent is then
removed, and the product is cooled and comminuted
if appropriate.

A 2.2 without solvent

20 The IPDI uretdione at a temperature of 60 to
110°C was fed into the intake housing of a twin-
screw extruder, the polyol component - see Table
2 - being metered in simultaneously at a tempera-
ture of 25 to 110°C. If appropriate the uretdione
and/or the polyol component contains the quantity
of catalyst required - from 0.03 to 0.5% by
25 weight of DBTL - based on the end product.

30 The extruder employed is composed of ten housings
of which five are heating zones. The temperatures
of the heating zones are subject to a wide range
- between 50 and 180°C - and can be controlled
individually. All of the temperatures are set-
point temperatures, with regulation in the
housings being carried out by electrical heating
and pneumatic cooling. The die element is heated

by means of an oil thermostat. The speed of the two screws, fitted with conveying elements, was between 50 and 380 rpm.

5

The reaction product, obtained in quantities of from 10 to 130 kg/h, is either cooled and then comminuted or shaped and bagged, or the actual melt is shaped, and the shaped articles are then cooled and bagged.

10

The physical and chemical characteristics of the process products of the invention and the molar compositions are summarized in Table 2.

The IPDI uretdione produced by the known process had the following NCO characteristics:

15

free: from 16.8 to 18.5% by weight
total: from 37.5 to 37.8% by weight

Table 2

Example A 2	Composition (mole)			Chemical and physical characteristics			
	IPDI uretdione	Diol(s)	Chain extender A 1	NCO content (% by weight)		Melting range °C	Glass transition temperature °C
				free	total		
1	(7)	Eg (8)	-	0	12.1	108 - 115	62 - 81
2	(7)	Eg (3), C ₁₂ (3), E (2)	-	< 0.1	12.8	110 - 113	65 - 87
3	(7)	Eg (4), B (4)	-	< 0.1	13.1	117 - 122	82 - 95
4	(7)	Eg (4), TMH-d (4)	-	< 0.1	12.5	101 - 103	56 - 72
5	(7)	Eg (6), Pm (2)	-	0	12.4	108 - 111	61 - 78
6	(8)	Eg (4), Pm (3), B (2)	-	0.1	13.1	106 - 114	58 - 75
7	(8)	TMH-d (6), B (3)	-	0.1	13.6	111 - 115	63 - 81
8	(9)	TMH-d (5), Pm (4), B (1)	-	< 0.1	13.8	113 - 118	66 - 84
9	(9)	Eg (4), TMH-d (3) B (2), E (1)	-	0.1	13.5	115 - 119	68 - 87

Table 2: continued

Example A 2	Composition (mole)			Chemical and physical characteristics		
	IPDI uretdione	Diol(s)	Chain extender A 1	NCO content (% by weight)		Glass transition temperature °C
				free	total	
10	(7)	B (4), E (2)	6 (2)	< 0.1	12.7	90 - 94
11	(7)	Eg (3.5) E (2.5) TMH-d (1.25)	6 (0.75)	< 0.1	12.1	105 - 108
12	(7)	Pm (6.5)	6 (1.5)	0	11.0	83 - 89
13	(7)	Eg (3.5), E (1) TMH-d (2.5)	7 (1)	< 0.1	10.1	81 - 86
14	(7)	Eg (3.5), HD (2) E (1.5)	6 (0.5) 7 (0.5)	0	11.5	91 - 94
15	(7)	Eg (3.5), E (3.5)	5 (0.5) 6 (0.5)	0	11.7	99 - 102
16	(6.5)	Eg (3), P (2) E (1.5)	5 (0.5) 6 (0.5)	0	11.9	101 - 108
17	(8)	Eg (4), TMH-d (1.25) Pm (2), E (1)	5 (0.5) 6 (0.25)	0.1	12.2	112 - 118

Table 3

Example A 2	Composition (mole)			Chemical and physical characteristics			
	IPDI uretdione	Diol(s)	Chain extender A 1	NCO content (% by weight)		Melting range °C	Glass transition temperature °C
				free	total		
1	(6)	B (1)	1 (6)	< 0.1	9.9	85 - 92	61 - 66
2	(7)	E (2)	1 (6)	< 0.1	10.8	88 - 91	53 - 67
3	(7)	E (4)	1 (4)	0	12.4	104 - 107	69 - 87
4	(7)	B (4.75)	1 (3.25)	0	12.2	102 - 104	70 - 85
5	(7)	TMH-d (7)	1 (1)	< 0.1	12.2	106 - 109	72 - 82
6	(7.5)	P (6.75)	1 (1.75)	0	13.1	104 - 111	72 - 91
7	(8)	Pm (7.75)	1 (1.25)	0	13.4	111 - 117	81 - 96
8	(7)	Pm (6.5)	2 (1.5)	< 0.1	12.3	112 - 115	75 - 90
9	(7.5)	E (6)	2 (2.5)	0	12.7	110 - 118	77 - 95
10	(7.5)	TMH-d (3) E (3)	2 (2.5)	< 0.1	12.3	108 - 115	71 - 86

Table 3: continued

Example A 2	Composition (mole)			Chemical and physical characteristics			
	IPDI uretdione	Diol(s)	Chain extender A 1	NCO content (% by weight)		Melting range °C	Glass transition temperature °C
				free	total		
11	(7)	TMD-d (6.5)	3 (1.5)	< 0.1	11.9	99 - 103	71 - 84
12	(8)	HD (6.5)	3 (2)	< 0.1	12.6	105 - 114	74 - 87
13	(7)	TMH-d (7)	4 (1)	0	12.2	99 - 102	74 - 90
14	(7.5)	B (5.5)	4 (3)	0	12.3	112 - 117	79 - 89
15	(8)	Pm (7)	4 (2)	< 0.1	12.6	109 - 117	75 - 92
16	(7)	Eg (3.25) Pm (3.25)	5 (1.5)	0	9.8	73 - 77	41 - 55
17	(7)	TMH-d (3.75) Eg (3.5)	5 (0.75)	0	10.2	90 - 93	53 - 76
18	(7)	Eg (5) E (2.5)	5 (0.5)	< 0.1	11.9	107 - 110	67 - 88

B Polyester

Table 4 below gives an overview of the polyesters on the market which are employed for the formulation of PUR powder coatings.

Table 4

Example B	Manufacturer country	Name of product	Chemical and physical characteristics				
			OH number mg KOH/g	Acid number mg KOH/g	Melting range °C	Glass transition temperature	Viscosity at 160°C mPa•s
1	Hoechst AG Italy	Alftalat AN 739	55 - 60	2 - 4	82 - 90	>50	24 - 29 000
2	DSM Netherlands	Uralac P 1460	38 - 41	4 - 4.5	70 - 75	50	40 000
3	UCB Belgium	Crylcoat 240	26 - 31	3 - 4	74 - 80	>50	33 - 38 000

C Polyurethane powder coatings

General preparation procedure

5 The comminuted products, crosslinking agents, polyesters, levelling agent masterbatch and, if desired, catalyst masterbatch are intimately mixed, together if desired with the white pigment, in an edge runner mill and then homogenized in an extruder at not more than 130°C. The
10 extrudate is then cooled, fractionated and ground in a pin mill to a particle size < 100 µm. The powder thus prepared is applied using an electrostatic powder spraying unit at 60 kV to degreased and - if appropriate - pretreated iron panels
15 which are baked in a circulating-air drying cabinet at temperatures of between 160 and 200°C.

Levelling agent masterbatch

10 per cent by weight of the levelling agent - a commercially available copolymer of butyl acrylate and 2-ethylhexyl acrylate - are homo-
20 genized in the melt in the corresponding polyester and, after solidifying, are comminuted.

Catalyst masterbatch

5 per cent by weight of the catalyst - DBTL - are homogenized in the melt in the corresponding
25 polyester and, after solidifying, are comminuted.

The abbreviations in the following tables denote:

	LT	= layer thickness in µm	
	KH	= König hardness (sec)	(DIN 53 157)
	BH	= Buchholz hardness	(DIN 53 153)
30	EI	= Erichsen indentation	(DIN 53 156)

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CH = crosshatch test (DIN 53 151)
GG 60 ° = gloss measurement according to
Gardner (ASTM-D 523)
Imp.rev. = impact reverse in g•m

Table 5

Pigmented powder coatings

Example C Formulation	1	2	3	4	5	6	7	8	9	10	11	12
Crosslink- ing agent acc. to A 2	25.98	20.84	14.5	26.44	21.36	24.83	13.76	24.97	26.13	20.97	14.6	27.07
Table 2 (Example) Polyester acc. to B 1	(2)	(2)	(2)	(4)	(5)	(7)	(7)	(9)	(10)	(10)	(10)	(11)
Polyester acc. to B 2	74.02	-	-	73.56	-	75.17	-	75.03	73.87	-	-	72.93
Polyester acc. to B 3	-	79.16	-	-	78.64	-	-	-	-	79.03	-	-
Polyester acc. to B 3	-	-	85.5	-	-	-	86.24	-	-	-	85.4	-
Notes:	All formulations contain 40% by weight of TiO ₂ (white pigment) and each contain 0.5% by weight of levelling agent and benzoin and 0.15% by weight of DBTL; the OH/NCO ratio = 1 : 1											
Coatings data												
LT	55-70	70-95	55-80	60-75	65-80	55-70	60-85	55-70	65-85	60-70	65-85	70-95
KH	192	200	193	194	191	197	195	192	188	184	186	186
BH	100	111	100	111	100	100	111	100	100	100	111	111
CH	0	0	0	0	0	0	0	0	0	0	0	0
GG 60 [°]	88-89	89-92	92-93	89-91	90-91	88-90	90-93	88-89	90	90-91	92-93	89-92
EI	>10	>10	>10	>10	9.5-9.8	9.7-10	>10	9.2-10	>10	>10	>10	10
Imp.rev.	>944.6	>944.6	>944.6	>944.6	806.4	806.4	>944.6	>944.6	>944.6	>944.6	>944.6	>944.6
Notes:	Curing conditions: 200°C/8 minutes or 180°C/15 minutes											

Table 6
Pigmented powder coatings

Example C Formulation	13	14 *	15	16 *	17	18	19	20	21	22	23	24
Crosslink- ing agent acc. to A 2	29	24.62	16.48	13.64	28.09	27.74	22.36	15.65	27.4	-	-	-
Table 2 (Example)	(12)	(12)	(12)	(12)	(14)	(15)	(15)	(15)	(17)			
Crosslink- ing agent acc. to A 2	-	-	-	-	-	-	-	-	-	31.21	29.38	16.74
Table 3 (Example)										(1)	(2)	(2)
Polyester acc. to B 1	71	75.38	-	-	71.91	72.26	-	-	72.6	68.79	70.62	-
Polyester acc. to B 2	-	-	-	-	-	-	77.64	-	-	-	-	-
Polyester acc. to B 3	-	-	83.52	86.36	-	-	-	84.35	-	-	-	83.26
Notes:	All formulations contain 40% by weight of TiO ₂ (white pigment) and each contain 0.5% by weight of levelling agent and benzoin and 0.15% by weight of DBTL; the OH/NCO ratio = 1 : 1, * OH/NCO = 1 : 0.8											
Coatings data												
LT	70-75	80-95	70-90	65-85	70-85	50-65	65-80	60-75	70-85	60-75	65-80	70-75
KH	188	186	185	183	183	182	184	185	181	182	180	187
BH	118	100	100	111	111	100	100	100	100	100	105	100
CH	0	0	0	0	0	0	0	0	0	0	0	0
GG 60°	89	90-91	92-93	93	89-90	88	89	92	89	89	88	91-92
EI	>10	>10	>10	>10	>10	>10	>10	9.3	9.9	>10	>10	>10
Imp.rev.	>944.6	>944.6	806.4	>944.6	691.2	576	806.4	576	691.2	>944.6	>944.6	>944.6
Notes:	Curing conditions: 200°C/8 minutes or 180°C/15 minutes											

Table 7
Pigmented powder coatings

Example C Formulation	25	26	27	28	29 O	30 *	31	32	33	34	35	36
Crosslink- ing agent acc. to A 2	26.59	14.9	25.58	25.53	25.53	21.53	20.46	14.22	21.5	26.01	17.55	22.06
Table 3 (Example)	(3)	(3)	(4)	(6)	(6)	(6)	(6)	(6)	(8)	(13)	(17)	(18)
Polyester acc. to B 1	73.41	-	-	74.47	74.47	78.47	-	-	-	73.99	-	-
Polyester acc. to B 2	-	-	74.42	-	-	-	79.54	-	78.5	-	-	77.94
Polyester acc. to B 3	-	85.1	-	-	-	-	-	85.78	-	-	82.45	-
Notes:	All formulations contain 40% by weight of TiO ₂ (white pigment) and each contain 0.5% by weight of levelling agent and benzoin and 0.15% by weight of DBTL; the OH/NCO ratio = 1 : 1, * OH/NCO = 1 : 0.8, 0.05% by weight DBTL											
Coatings data												
LT	75-90	75-85	65-80	60-75	65-75	50-55	55-75	70-75	60-80	50-70	50-65	60-70
KH	185	188	184	184	184	182	184	185	183	185	186	184
BH	105	100	100	100	100	111	100	100	100	100	100	100
CH	0	0	0	0	0	0	0	0	0	0	0	0
GG 60°	88-89	90-91	89	88-89	89	90	89-90	91-92	89-90	88-89	90-91	89-90
EI	>10	>10	>10	>10	9.1-10	>10	>10	>10	>10	>10	>10	9.4-10
Imp. rev.	806.4	691.2	944.6	>944.6	691.2	>944.6	>944.6	>944.6	>944.6	>944.6	>944.6	806.4
Notes:	Curing conditions: 200°C/8 minutes or 180°C/15 minutes											

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A polyaddition product containing hydroxyl and uretdione groups and prepared from a uretdione of isophorone diisocyanate with a diol or a chain extender, obtainable by reacting
 - I. from 40 to 85% by weight of the uretdione of isophorone diisocyanate and
 - II. from 60 to 15% by weight of a diol or a chain extender, the polyaddition product carrying terminal hydroxyl groups, having a functionality of 2 and a molecular mass of between 4,500 and 10,000.
2. A polyaddition product containing hydroxyl and uretdione groups according to claim 1 having a molecular mass of between 4,500 and 7,000.
3. A polyaddition product containing hydroxyl and uretdione groups according to claim 1, wherein the diol is selected from the group consisting of ethylene glycol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentane-1,5-diol, 2,2,4(2,4,4)-trimethylhexanediol (isomer mixture) and neopentylglycol hydroxypivalate.
4. A polyaddition product containing hydroxyl and uretdione groups according to claim 1, wherein the chain

extender is a linear polyester containing hydroxyl groups having a molecular mass of between 250 and 2,000.

5. A polyaddition product containing hydroxyl and uretdione groups according to claim 4 wherein the linear polyester has a molecular mass of between 300 and 1,500.
6. A polyaddition product containing hydroxyl and uretdione groups according to claim 4, wherein the linear polyester containing hydroxyl groups is composed of at least one monomer in each case selected from the group consisting of ethylene glycol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentane-1,5-diol, 2,2,4(2,4,4)-trimethylhexanediol and neopentylglycol hydroxypivalate, 2-methylpropanediol, 2,2-dimethylpropanediol, diethylene glycol, dodecane-1,12-diol, trans-and cis-cyclohexanedimethanol and succinic, adipic, suberic, azelaic, sebacic, and 2,2,4(2,4,4)-trimethyladipic acid (isomer mixture), ϵ -caprolactone and hydroxycaproic acid.
7. A polyaddition product containing hydroxyl and uretdione groups according to claim 1 comprising a diol/chain extender mixture in a ratio of from 5 : 95 to 90 : 10.
8. A polyaddition product containing hydroxyl and uretdione groups according to claim 1, wherein the reaction of the uretdione of isophorone diisocyanate and the diol or chain

extender is carried out in solvent, which is removed after reaction has taken place.

9. A polyaddition product containing hydroxyl and uretdione groups according to claim 1, wherein the reaction of the uretdione of isophorone diisocyanate and the diol or chain extender is carried out without solvent in intensive kneading apparatus.

10. A polyaddition product containing hydroxyl and uretdione groups according to claim 9 wherein said intensive kneading apparatus is a twin-screw extruder.

11. A polyaddition product containing hydroxyl and uretdione groups according to claim 1, wherein a catalyst is employed in a concentration of from 0.01 to 1% by weight of reactants.

12. A polyaddition product containing hydroxyl and uretdione groups according to claim 11 wherein said catalyst is an organotin compound.

13. A polyaddition product containing hydroxyl and uretdione groups according to claim 11 wherein said catalyst comprises from 0.03 to 0.5% by weight of reactants.

14. A process for preparing a polyaddition product, containing hydroxyl and uretdione groups which process comprises reacting
- I. from 40 to 85% by weight of uretdione of isophorone diisocyanate and
 - II. from 60 to 15% by weight of a diol or a chain extender, at a temperature of from 50 to 100°C in a solvent which is removed after the reaction has taken place, or without a solvent in intensive kneading apparatus at a temperature of from 120 to 190°C.
15. A process according to claim 14 wherein said intensive kneading apparatus is a twin-screw extruder.
16. A process according to claim 14 when carried out in the presence of a catalyst comprising from 0.01 to 1% of reactants.
17. A process according to claim 14, wherein the chain extender is a linear polyester containing hydroxyl groups and having a molecular mass between 250 and 2,000.
18. A process according to claim 17 wherein said linear polyester has a molecular mass between 300 and 1,500.
19. Use of a bifunctional polyaddition product free from a blocking agent and containing hydroxyl and uretdione groups, according to any one of claims 1 to 15, in combination with a

polymer containing hydroxyl groups, for production of transparent or pigmented, highly reactive polyurethane powder coatings which are free from elimination products.

20. Transparent or pigmented polyurethane powder coating free from elimination products, comprising a bifunctional polyaddition product free from a blocking agent and containing hydroxyl and uretdione groups, according to any one of claims 1 to 13, in combination with a polymer containing hydroxyl groups, and a coating acceptable additive or auxiliary.
21. A polyurethane powder coating according to claim 20, having an underlying OH/NCO ratio from 1 : 0.5 to 1 . 2.
22. A polyurethane powder coating according to claim 21 wherein the underlying OH/NCO ratio is from 1 : 0.8 to 1 . 1.
23. A polyurethane powder coating according to claim 21 wherein the underlying OH/NCO ratio is about 1 : 1.
24. A polyurethane powder coating according to claim 20 wherein a catalyst is added to polyurethane powder coating in a concentration of from 0.03 to 0.5% by weight, when including any catalyst already present following the reaction of the uretdione of isophorone diisocyanate and a diol or chain extender.

25. A polyurethane powder coating according to claim 24 wherein said catalyst is an organotin catalyst.
26. A polyurethane powder coating according to claim 24 wherein 0.05 to 0.15% by weight of catalyst is added to the polyurethane powder.
27. A polyurethane powder coating according to claim 20 wherein the hydroxyl group-containing polymer employed is a polyester having a functionality > 2 , an OH number of from 20 to 200 mg of KOH/g, a viscosity $< 60,000$ mPa·s at 160°C , and a melting point $\geq 70^{\circ}\text{C}$ and $\leq 120^{\circ}\text{C}$.
28. A polyurethane powder coating according to claim 27 wherein said polyester has an OH number of from 30 to 150 mg of KOH/g, a viscosity of greater than 40,000 mPa·s at 160°C and a melting point of 75°C to 100°C .
29. Use of a polyurethane powder coating according to any one of claims 20 to 28 for application to a substrate for a heat-curable coating.

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